CHEMICAL AND INFRARED STUDIES ON THE STRUCTURE OF CERTAIN COMPOUNDS CONTAINING SILICON-NITROGEN BONDS

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1949

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1950

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INTRODUCTION

A survey of the available literature on organic silicon compounds disclosed that a great amount of work has been done by many of the investigators within and without the field of organic chemistry. A careful study of the historical progress of organic silicon chemistry revealed an uncertain road toward the ultimate goal which seemed to be the establishment of a new chemistry as versatile as carbon chemistry.

The American Chemical Society has given serious study to the matter of the nomenclature of organic compounds of silicon. As a result, there recently appeared three important publications (1, 13, 16). To date the nomenclature is an open matter and the system preferred varies with different investigators of silicon compounds. For use in this thesis, a system similar to that proposed by Stock (18, 19, 20) was used. It was believed that this system, when used in reference to the compounds herein discussed, produced the most euphonic and least ambiguous terminology. Stock preferred the use of the root name of silane for SiH_4. Silicon compounds would thus be named as derivatives of this fundamental term, such as tetrachlorosilane for $SiCl_4$, commonly called silicon tetrachloride. One of the compounds discussed later has the formula $Si(NHC_6H_5)_4$, and would thus be named tetraanilinosilane. This system will be followed throughout this thesis except where alteration of direct quotations would decrease their value.

In The Bakerian Lecture of 1937, Kipping (10) stated:

The discovery of tetrachlorosilane by Berzelius in 1823 might have led to an immediate advance; but it was not until 23 years later that this compound was used by Ebelmen for the preparation of the first organic silicon compound, ethyl orthosilicate, $Si(OEt)_4$. This ester, produced by the interaction of alcohol and tetrachlorosilane, was, however, completely decomposed by water and seemed to be of such little use for the preparation of other substances that a further 17 years elapsed before any progress was made.

The first compound in which carbon and silicon atoms were united directly was prepared by Friedel and Crafts (6) in 1863 by the action of zinc alkyls on tetrachlorosilane. The tetraalkylsilanes obtained, unlike the previously mentioned compounds, were extremely stable and, therefore, seemed to offer hope of use in other investigations.

In the following decades many organic investigators, among whom must be mentioned Friedel, Ladenburg, and Polis, synthesized many new organic silicon compounds. This seemed to point the way of expansion to new methods analogous to those used in organic chemistry. Great strides in the development of this new chemistry took place during these years, but eventually these investigators found many anomalous comparisons when too close an analogy was drawn to organic chemistry.

This was the state of progress Kipping found in 1899 when he began a systematic investigation of the general field. Kipping noticed that by way of general comparison of carbon with organic derivatives of silicon that many, if not most, of the more important types of the former are not represented among the latter. It became apparent to investigators that this was not merely a

consequence of insufficient experimental investigation on silicon derivatives, but rather due to fundamental differences in the properties of the atoms of silicon and carbon.

In spite of this, the development of new methods came rapidly and was then followed by periods of comparative inactivity. At present there are several thousand organic silicon compounds which have been prepared--the recent, rapid progress perhaps being catalyzed by the large, potential, industrial demand for such materials.

It was thought that additional information on the nature of silicon bonding might be useful in preventing a future stalemate in the preparation of new silicon compounds. Therefore, an investigation was undertaken concerning the silicon-nitrogen-carbon series of bonds. This phase of study had more or less been neglected, almost since the time the first bonds of this type were established around 1883 (21). Perhaps this may be explained by the fact that, with very few exceptions, such compounds have no industrial application. This feeling was manifested more recently in 1936 during The Bakerian Lecture by Kipping (10). He stated, in part:

> Very few substances containing silicon and nitrogen atoms directly united have been prepared since it was shown by E. Reynolds that silicontetraphenylamide, $Si(NHPh)_4$, is completely decomposed not only by water but also by alcohol. Even when a molecule contains only one silicon-nitrogen link it is still very unstable towards water and although certain compounds of this type have been prepared from the chlorides, SiR_3Cl, they are of little interest.

The evidence of E. Reynolds to which Kipping referred was published in 1889 (15). He reported a violent and exothermic reaction when tetrachlorosilane was reacted with aniline in a benzene solution with the formation of one equivalent of tetraanilinosilane (m.p. 137° to 138°) and four of aniline hydrochloride.

This same reaction had been investigated by Harden (7) in 1887. He reported the production of one equivalent of dianilinodichlorosilane and two of aniline hydrochloride.

At first these results seemed in disagreement, but upon careful reproduction of the original experiments by this author, it became apparent that Harden used an insufficient quantity of aniline to produce the tetra-substituted product. Thus Harden's product was, in all probability, the di-substituted tetrachlorosilane as was reported.

During a preliminary search of compounds suitable for use in this thesis, several silicon-nitrogen compounds were prepared. An attempt was made to combine aniline, pyridine, dimethyl aniline, benzamide and urea with tetrachlorosilane. Of these, the compound which was formed when tetrachlorosilane and aniline were reacted seemed to be the most stable with respect to atmospheric water vapor and, therefore, suggested the logical starting place for investigation. It was proposed that the aniline combined with the tetrachlorosilane according to the following equation.

$$SiCl_4 + 8\ C_6H_5NH_2 = Si(NHC_6H_5) + 4\ C_6H_5NH_2 \cdot HCl$$

PURIFICATION OF CHEMICALS

The benzene was shaken in a separatory funnel with several portions of concentrated sulfuric acid to remove any thiophene that might have been present. After the benzene was thoroughly washed with water, it was distilled twice and dried over sodium wire for at least one week.

The aniline as purchased was certified pure. This aniline was distilled with only the center fraction being retained for use in the following preparations. It was then dried over potassium hydroxide pellets for two days. The dried aniline was filtered into a distilling flask containing a small portion of zinc dust and was slowly distilled. After the resulting water-white aniline stood for a day, some zinc dust settled to the bottom of the receiver. This entrained zinc dust proved very difficult to separate completely from the colorless aniline. Many subsequent distillations were necessary. This process might have been considerably shortened by the use of a packed distilling column with a high reflux ratio. The resulting aniline did not discolor when exposed to light for a considerable period of time, but it was found to be advisable to store the aniline in a brown bottle if not intended for use within a week.

The carbon bisulfide as manufactured probably contained many impurities. Crude carbon bisulfide was shaken with mercuty in a separatory funnel until film no longer formed on the surface of the mercury. During this process the film separated fairly well

from the mercury, and the mercury was drained from the funnel. A cold saturated solution of mercuric chloride and the remaining carbon bisulfide was shaken together for 15 minutes. After the aqueous layer was drained off, the same process was followed with a saturated solution of potassium permanganate. The resulting wet carbon bisulfide was dried over phosphorous pentoxide and then carefully distilled. Utmost care must be exercised when distilling carbon bisulfide! It is extremely flammable and has been known to ignite and explode even when being heated on a steam bath. The boiling point of carbon bisulfide is 42.2° C. and consequently it is possible to overheat this explosive liquid during distillation. In this investigation all apparatus connections were constructed of ground glass joints and carefully checked for leaks. The necessary heat was supplied by a non-explosive type heating mantle. The carbon bisulfide in the distilling flask was maintained at a gentle boil by use of coconut charcoal boiling chips.

According to diagrams published by Schwartz and Meyer (17), there should be only a negligible quantity of hydrogen chloride dissolved in the tetrachlorosilane at room temperature and pressure. It was decided, therefore, that a simple fractional distillation in an all glass apparatus was sufficient for purification of the tetrachlorosilane. This was carried out in an especially designed distillation apparatus in which only two small ground glass openings were provided--one for the introduction of the crude material and one for the removal of the middle fraction of distillation as shown in Fig. 1. The receiver was

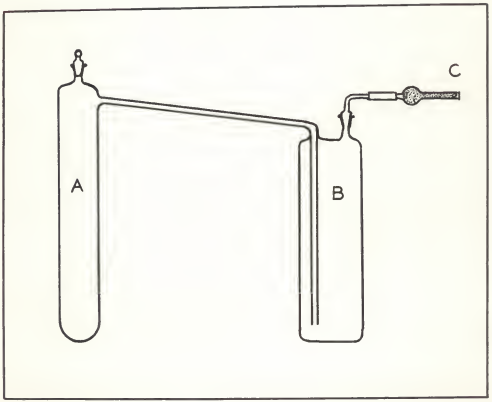


Fig. 1. Distillation apparatus for tetrachlorosilane: A, distillation flask; B, receiver; C, drying tube.

placed in an ice bath to insure condensation of all vapors. The freezing of ground glass joints in the presence of tetrachlorosilane presented an ever present problem. This problem was never completely solved. As soon as use of the apparatus was terminated, it was swept dry with dry air. The best lubricant proved to be silicone grease.

The monomethyl aniline was dried over potassium hydroxide and then distilled until a dark yellow liquid appeared.

EXPERIMENTAL

The Preparation of Tetraanilinosilane

The reaction vessel used was a three liter, three-neck, round bottom flask. Through the center neck was placed a mechanical stirring device with large glass blades. Another opening held a thermometer. A separatory funnel was placed through the third opening. The assembled apparatus was set into an ice salt water bath. Four hundred and thirty-eight grams of aniline were weighed into more than twice its volume of dry benzene. After this mixture was transferred into the reaction vessel, it was allowed to cool to 5° C. One hundred grams of tetrachlorosilane were weighed into five hundred milliliters of benzene and then transferred into the separatory funnel.

The reaction began as soon as the tetrachlorosilane dropped onto the aniline in the reaction vessel. The mechanical stirrer had to be maintained at maximum speed in order to achieve the

desired mixing. The addition of tetrachlorosilane was controlled so that the maximum temperature of the reacting mixture did not rise above 20° C. An immediate rise in temperature resulted as soon as several drops of the tetrachlorosilane reacted. The entire reaction was highly exothermic thus necessitating a very slow rate of addition of the reactant. Approximately two hours were required for the addition of all of the tetrachlorosilane.

After one-fourth of the reactant had been added, the reaction mixture turned almost solid due to the formation of large volumes of white aniline hydrochloride as a by-product. When one-half of the tetrachlorosilane had been added, the mixture became almost impossible to stir. Benzene was added in sufficient quantity to maintain the aniline hydrochloride as a suspension.

As soon as all of the reactants were combined, the ice bath was removed and the reacting mixture was allowed to reach room temperature. The semi-solid mixture was filtered in a large Buchner funnel in an attempt to separate the aniline hydrochloride from the product. The mixture filtered very slowly and aniline hydrochloride seemed to cloud the filtrate. This difficulty was encountered during many successive filtrations and purifications. The aniline hydrochloride was washed with dry benzene and the clear solution was added to the filtrate.

The filtrate, which held the product in solution, was transferred to a large distilling flask. This flask was assembled so that during distillation dry hydrogen swept the entire system. The stream of hydrogen was directed onto the surface of the liquid

in the distilling flask. Care must be exercised in the disposal of waste gases issuing from the far end of the condenser since these gases might contain an explosive mixture of hydrogen, benzene and some unknown low-boiling products. An electric mantle provided the heat necessary for distillation. All products which would distill, under these conditions at vapor temperatures up to 100° C. were removed. The distillate thus contained all of the benzene and some aniline.

When the distilling flask was allowed to cool, a resinous mass solidified. In appearance the residue closely resembled a perfectly clear, amber-colored plastic. No indication of crystalline structure could be found. The residue appeared to expand upon solidification. The flask had to be rotated in a swirling motion during cooling to prevent any cracking of the vessel.

A portion of this solid was placed in a small bottle and irradiated for some time with a commercial photo-flood bulb. The solid went through successive color changes exactly analogous to those of a bottle of pure aniline placed next to the sample. This indicated that the solid must contain some included aniline since no proof could be found that pure tetraanilinosilane was light sensitive.

The remaining solid was placed in a 50 ml distilling flask. The distillation was carried out until a pot temperature of 210° C. was reached. From this solid was distilled an oily liquid which proved to be the light sensitive contaminate, aniline. The residue of this distillation was dissolved in carbon bisulfide. A

very fine powder of aniline hydrochloride became suspended in the solution. The solid was filtered only after repeated attempts with the finest filter paper.

Reynolds reported (14), that:

> . . . evaporation of the solution leads to the separation of magnificent crystals of the silicon compound . . . The crystals of silicotetraphenylamide (tetraanilinosilane) are perfectly colorless short prisms of considerable size. They melt at 136-137° to a transparent liquid, which can be heated to 210° without decomposition. On cooling this liquid solidifies to a transparent glass which, like the original crystals can be easily decomposed by water.

Actually, the crystallization was not found to be as easy as described by Reynolds. Over six months were spent in an attempt to obtain pure crystals of the product by varying the concentration and temperature, by seeding and by the use of various solvents and solvent pairs. A fine powder was ultimately separated from the carbon bisulfide solution after the addition of petroleum ether. A few absolutely perfect 90° cubic crystals were formed. These were separated from the white powder with the aid of a microscope. Unfortunately these crystals were destroyed when placed in contact with some petroleum ether that was not absolutely dry. The white powder was filtered from the carbon bisulfide and redissolved in the same solvent. After this process was repeated several times, the final solution was concentrated by careful evaporation of the solvent under reduced pressure. Within several days small clear crystals were formed. These were stored under dry petroleum ether. A portion of these crystals were redissolved and placed in a covered, crystallizing dish in a

desiccator. Small crystals were formed and these grew into larger ones.

The Preparation of Tetra-N-methylanilinosilane

During several preliminary experiments, it was found that monomethylaniline combined with tetrachlorosilane very rapidly in anhydrous ether, at a moderate rate in carbon bisulfide while no apparent reaction took place in benzene solution. It was decided that carbon bisulfide would serve as a convenient medium in which to conduct the reaction. This solvent does not dissolve the hydrochloride salt; it is easily removed from the product by means of reduced pressure; and it has spectral properties which proved important in later experiments.

Eight moles of monomethylaniline were diluted with twice its volume of carbon bisulfide. One mole of tetrachlorosilane was diluted with twice its volume of carbon bisulfide and added slowly to the monomethylaniline mixture. During the addition of the first half of the reactants, a white precipitate fell to the bottom of the reaction flask. However, as more reactants were combined, the precipitate appeared to vanish. Upon completion of the reaction, the mixture was filtered and considerable crystalline precipitate filtered out. Successive filtrations separated more of the monomethylaniline hydrochloride from the mixture. The carbon bisulfide was removed at room temperature by means of reduced pressure. The product was then in the form of a clear, amber-colored, putty-like plastic.

No attempt was made to crystallize this product since the very small amount of contaminant present did not exert appreciable influence during spectral analysis.

Analysis of Tetraanilinosilane

Physical Constants. A portion of the crystals were powdered under dry petroleum ether. The petroleum ether was removed by means of reduced pressure at room temperature. The dry powder was transferred to a thin walled, capillary tube and placed in a modified Thiele melting point apparatus. The melting point corresponded to the 137--138° C. range reported in the literature for $Si(NHC_6H_5)_4$ (15). Approximately 22 grams of the compound were contained in 100 grams of carbon bisulfide solution at room temperature.

Percentage Nitrogen. One-half gram of powdered tetraanilinosilane was accurately weighed into 250 ml of benzene. Three ml of this solution were measured into a 20 ml micro-Kjeldahl flask that contained one droplet of mercury as a catalyst. This solution was digested with three ml of concentrated sulfuric acid for 30 minutes and allowed to cool. Six drops of 30 percent hydrogen peroxide were added and the digestion continued for 10 minutes. After the digested mixture cooled, five ml of water were cautiously added. This solution was transferred to the micro-Kjeldahl apparatus described in Niederl and Niederl (12) and 15 ml of 30 percent sodium hydroxide solution were added. The digestion flask was rinsed with 10 ml of water and the rinse

solution was poured into the micro-Kjeldahl apparatus. Steam was then allowed to bubble through the mixture. The steam distillation continued for four minutes after the silver tube condenser at the end of the apparatus began to heat. The distillate was caught in 5 ml of 5 percent boric acid solution to which one drop of indicator had been added. The boric acid solution was removed from the condenser at the end of the four minute period and titrated against standardized acid.

The average result of five determinations showed that the nitrogen content was 13.62 percent against a theoretical value of 14.14 percent. A possible explanation for this low result will be discussed in the following pages.

Percentage Silicon (Method I). One-half gram of sample was weighed into a dried, weighed, micro-Kjeldahl flask. This flask had four baffles in its neck in order to prevent the passage of light flakes of silicon dioxide during strong heating. A few drops of concentrated nitric acid were added. After the initial reaction subsided, about five ml of concentrated sulfuric acid were added. This mixture was very cautiously heated over a low flame until it ceased to froth. After the flask cooled, a 50--50 mixture of 30 percent hydrogen peroxide and concentrated nitric acid was added and the mixture again cautiously heated. Additional quantities of the nitric acid-hydrogen peroxide mixture were added whenever it was necessary to prevent charring in the reaction flask. When the mixture ceased to char under strong heating, and without the addition of the oxidizing agent, the remain-

ing acid was fumed off and the micro-Kjeldahl flask was strongly heated to a dull red color until no more acid fumes appeared at the mouth of the flask. A fine white powder of silicon dioxide remained in the bottom of the flask. After the flask cooled, it was again weighed and the percent silicon in the sample was calculated from the weight increase of the flask. By this method the sample was found to have given an average value of 8.17 percent for silicon against 7.08 percent as a theoretical value. This high result will be discussed in the following pages.

Qualitative Test for Chlorine. An analysis for chlorine was made to determine whether all of the chlorine in the tetrachlorosilane had been replaced by aniline. The sodium fusion and the potassium carbonate-magnesium fusion methods were used as described by McElvain (11). Both methods gave a negative test for halogens.

Percentage Silicon (Method II). The poor results obtained by a previous method of analysis for silicon were considered and it was decided to attempt the analysis under different conditions. A 0.2 gram sample was weighed into a fired, porcelain, combustion boat. This boat was placed in a standard macro-combustion analysis apparatus and the sample burned very slowly. Low values for the silicon content were found to be the result of a quick ignition. As soon as the residue in the boat appeared to be the same color as clean white porcelain, the boat was removed from the furnace and allowed to cool in a desiccator. When cool, the boat was weighed and the percent silicon in the sample was calcu-

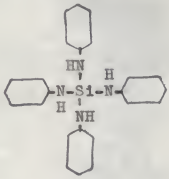
lated from the weight of the residue. This method gave a value of 6.98 percent silicon against a theoretical value of 7.08 percent.

Percentage Hydrogen and Carbon. The hydrogen and carbon content of the sample was determined by the standard macro-combustion method as described in Fisher (5). Hydrogen was found to be present as 6.10 percent of the total weight compared to 6.06 percent, the theoretical value. Carbon was found to constitute 72.48 percent of the sample. Theoretical carbon content was calculated to be 72.73 percent.

Molecular Weight Determination. The molecular weight of the compound was determined by the Beckmann Method of freezing point lowering in a benzene solution. In a typical analysis 0.5541 gram of sample in 12.3200 grams of benzene caused a freezing point depression of 0.576° C. The freezing point constant used in these calculations was 5.12°. The benzene was first dried over sodium and purified by repeated distillation. The distillate was then fractionally crystallized many times until only 500 ml of the original five liters of benzene remained as the pure solvent. The use of this benzene for the above determinations gave molecular weights of practically no deviation. The average value of these results gave a molecular weight of 395.00 for the compound. The theoretical molecular weight was calculated to be 396.92.

Conclusions from Analytical Data. From the results of the aforementioned analysis, the empirical formula was calculated to

be $C_{24}H_{24}N_4Si$. Upon hydrolysis this compound yielded aniline and silicon dioxide. It was concluded that the true molecular formula must be $Si(NHC_6H_5)_4$. The following structural formula was considered as representing the above empirical formula.



Discussion of Deviations in Analytical Data

The micro-Kjeldahl method of analysis for nitrogen yielded a value constantly below that which was calculated theoretically. At the time this particular analysis took place, the only micro-Kjeldahl apparatus available was one regularly used for feed analysis. The standard acid used in titrating the distillate was standardized against a feed sample of known nitrogen content instead of a primary standard. This procedure automatically corrected all errors inherent in feed analysis but possibly caused an incorrect result in silicon-nitrogen analysis.

Since an extremely vigorous oxidation was necessary during the Kjeldahl digestion, it is possible that some nitrogen containing substance was carried out of the digestion flask causing a low result.

INFRARED SPECTROSCOPY

Introduction

In recent years infrared spectroscopy has proved to be an important tool in industrial and academic research. Proper application of spectrometric methods yields much desirable information on the structural and thermodynamic properties of the molecule in question. Since much information was needed in order to understand the nature of the silicon-nitrogen bond, it was decided to undertake an infrared study of that bond as found in the compounds described in the preceding pages.

The instrument used in this investigation was the Perkin-Elmer Infrared Spectrometer Model 12 A that was equipped with a gear driven, automatic wave-length selector coupled with a micrometer slit width control. A standard sodium chloride prism was used in the range of 1 to 15 microns. The transmitted radiation was detected by a vacuum thermocouple, amplified and recorded by a Leeds and Northrup Speedomax type G recorder.

The cell containing the sample was placed in the light path at the position designated as C in Fig. 2. The cell consists of two flat sodium chloride plates placed in a holder. The sample to be analyzed was placed between the two plates and the plates were then clamped together. The thickness of the sample was considered to be capillary. Generally speaking, infrared characteristics are retained in solution thus offering a convenient

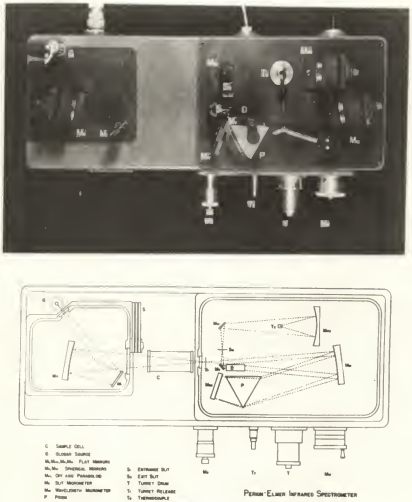


Fig. 1. Top view photograph and diagrammatic sketch of Perkin-Elmer Infrared Spectrometer with protective covers removed.

means of attaining the transparent film necessary for an analysis.

The usefulness of infrared spectroscopy is dependent upon the fact that compounds exhibit selective absorption in the spectral region of 1 to 100 microns. When an incident beam of light of all wave-lengths strikes a thin film of molecules, some wavelengths will be absorbed and some will pass through unaltered. Light absorption of a particular wave-length occurs only if the molecules are capable of rearrangement of their possible motions in such a way as to utilize the energy represented by that wavelength. There are three important ways in which a molecule may adjust its intramolecular configuration in such a way as to take up the energy of incident light by quantized increments. The energy absorbed by the molecule may be used to cause motion of the electrons from one energy level to another. Secondly, energy may be utilized to cause atomic nuclei to modify their positions relative to one another without changing the center of gravity of the group as a whole. This is generally called vibrational motion. The third method of energy utilization employs light of relatively lower energy content to cause molecules to rotate as a unit. These three methods describing how light may be absorbed are listed in order of decreasing energy. The energies absorbed by use of the first method are generally associated with the ultraviolet spectrum and, therefore, will not be of major interest in this discussion. The concept of energy absorption by the second and third methods is used to derive expressions for interpretation of near infrared (1 to 50 microns), far infrared

(50 to 100 microns) and Raman spectra. Although Raman lines may occur in the same frequency range as infrared lines, due to the different mechanism involved, lines may also be observed which are due to transitions not permitted in the direct absorption or emission of radiation involved in infrared spectra. The Raman effect involves a photon collision with a molecule in which there is an interchange of energy. In such a collision, the molecule absorbs energy and it is thus raised to a higher energy level after which it emits radiation and returns to a lower energy level, but not necessarily to the same level as the initial state. Thus the scattered radiation has a slightly different frequency than the incident beam. The difference in energy between the incident and scattered light is equal to the change in molecular energy and is known as a Raman shift. These frequency shifts are of the order of 100 to 4,000 $cm.^{-1}$ and many are equal to frequencies found in infrared absorption. Although a Raman spectrometer was not available, it was hoped that other investigators might combine the infrared data contained in this thesis to yield further information.

A molecule will exhibit absorption in the infrared region only if its electrical configuration is able to change relative to a point in space. This means that an infrared active vibration will result only if the electric moment of the molecule changes during that vibration. The same is true of absorption due to rotation. For the present we will consider the diatomic molecule as being represented analogically by two spheres in space joined

together by a coil spring. These two bodies will obey the classical laws of harmonic oscillators. If these two spheres were allowed to come to rest, they would arrange themselves so as to require the minimum potential energy. The configuration of such a system is known as equilibrium position. However, at room temperature the atoms of all molecules are constantly oscillating about their equilibrium positions. The frequency of such oscillations in a molecule are a function of the atomic masses, the strength of the atomic bonds and the geometric configuration of the molecule. The order of magnitude of these frequencies of vibration and rotation corresponds to infrared radiation. Experiments have demonstrated that certain atomic groups give rise to absorption of a specific nature, irrespective of the molecules in which they occur. Therefore, an infrared spectrum offers direct information as to the specific atomic linkages present. That is, since no two compounds have identical structures, their infrared spectra must differ, giving a unique "fingerprint" of a molecule.

If we consider one electronic energy level only, and allow a change to take place in the vibrational energy, the energy difference would be of the order of 1.6×10^{-13} erg per molecule. Quantum theory requires that the corresponding spectral lines have an approximate frequency of 2.5×10^{13} vibrations per second which correspond to a wave-length of 12 microns. This means that the radiations of purely vibrational changes in energy should appear in the near infrared region of the spectrum. In practice it is found that a vibrational transition is always accompanied by

rotational energy changes. This combination produces groups of closely spaced lines in the wave-length region of 1 to 23 microns. The ordinary laboratory spectrometer does not have the ability to separate these discrete energy absorptions and as a consequence they appear as absorption bands.

Derivation of Equations

Hooke's law states that a harmonic oscillator is one in which the restoring force is proportional to the displacement. If this is the case, the energy E_v of a harmonic oscillator in reciprocal centimeters is, according to quantum mechanics, given by equation 1 as derived in Herzberg (9).

(1) $$E_v = (v + 1/2)\omega_e,$$

where v is the vibrational quantum number which may be zero or an integer, and $\omega_e cm^{-1}$ is the equilibrium frequency of the oscillator for small displacements. It is generally found that these oscillators are not strictly harmonic. It is then necessary to add a term to correct for this deviation from ideal behavior. This "anharmonicity constant" x_e is included in the following manner:

(2) $$E_v = (v + 1/2)\omega_e - (v + 1/2)^2 x_e \omega_e.$$

Where anharmonic oscillators are considered, new selection rules are found which permit the appearance of additional bands. In order to recognize these bands it is necessary to define the fundamental frequency as one produced when the vibrational energy of a molecule changes from the initial level in which v is 0 to

that in which v is 1.

The energy change is derived from (2) as $E_1 - E_0 = (1 - 2x)\omega_e$. The frequency of the corresponding spectral line ω which is the center of the fundamental band is given by

(3) $$\omega = (1 - 2x)\omega_e.$$

If we consider a transition in which the initial value of v is 0 and the final value is 2, the frequency of the center of the first overtone band is then $(1 - 3x)2\omega_e$. If the substituted equations for the first, second, and third overtones are considered, it is apparent that the respective overtone bands are approximately in the ratio of 1 to 2 to 3. The wave-lengths are then in the proportion of 1 to 1/2 to 1/3. The overtone bands appear in the region of shorter wave-lengths and may be more easily studied.

As a first approximation, the anharmonicity of the oscillators may be neglected. Then for harmonic motion it is possible to write

(4) $$2\pi\omega_e c = (k/\mu)^{1/2},$$

where k is the restoring force per centimeter displacement acting between the nuclei and μ is the reduced mass. If the equilibrium vibrational frequency is known from measurements of the vibration-rotation bands, then the restoring force, or force constant, can be calculated. The force constant is related to the potential energy V of the vibrating system by the equation

(5) $$V = 1/2\ k(\Delta r)^2$$

where V is the potential energy and Δr is the change in the interatomic distance from its equilibrium value. If the numerical

values of the proper universal constants are substituted in equation 4, the dimensional formula is reduced to

(6) $$\omega_e = 1307\ (k/\mu)^{1/2} \text{cm.}^{-1},$$

where k is used as a pure number and μ is expressed in dimentionless atomic mass units.

The value of k for a single bond generally is found to be between 4 and 6 x 10^5 dynes per centimeter. The value for a double bond lies between 8 and 12 x 10^5 dynes per centimeter, while that for a triple bond generally lies between 12 and 18 x 10^5 dynes per centimeter.

Experimental data have shown that the value of k usually increases for an increase in the distance of equilibrium between the atoms under consideration.

Herzberg (8) stated that the bond force constant is more characteristic of a specific bond than the frequency. If the force constant of bonds in two molecules are the same, it may be said that the same bonds are present in both molecules. We could not necessarily draw the same conclusion if the same frequency was found to be present in both molecules.

If equation 2 is differentiated with respect to v in the same manner as Birge and Sponner (4), one may arrive at an equation by which may be used to calculate the energy of dissociation of the bond in question.

(7) $$dE_v/dv = \omega_e - 2(v + 1/2)x_e\omega_e.$$

At the convergence point $v = n_c$ and $dE_v/dv = 0$. Substituting n_c in place of v and setting the first derivative equal to zero, we

get

(8) $$\omega_e - 2(n_c + 1/2)x_e\omega_e = 0.$$

Rearrangement of the equation gives

(9) $$\omega_e = 2(n_c + 1/2)x_e\omega_e$$

(10) $$1 = 2(n_c + 1/2)x_e = 2x_e n_c + x$$

(11) $$2x_e n_c = 1 - x$$

(12) $$n_c = (1 - x)/2x_e$$

(13) $$n_c = 1/(2x_e) - 1/2 \quad \text{therefore}$$

(14) $$E_{n_c} = \omega_e\ (1/2\ x_e - 1/4\ x_e)$$

The energy of the limiting frequency is then given by

(15) $$E_{n_c} = \omega_e/4x_e.$$

The energy required to bring about dissociation of the molecule is the difference between E_{n_c} and the amount of energy initially possessed by the molecule. If this latter is assumed to be the zero point energy, then the energy of dissociation D in ergs per molecule is given by the equation $D = (E_{n_c} - E_0)hc$. Thus

(16) $$D = hc\omega_e/4 - (1/2\ hc\omega_e - 1/4\ xhc\omega_e).$$

This must be multiplied by the Avogadro number to obtain the energy of dissociation per mole.

Empirical observations led to the concept of valence and deformation vibrations. In every bond there is a vibration in which the bond is stretched, and another vibration of smaller frequency in which it is bent. For clarification consider the series of groups C-H, O-H and N-H in which it may be seen that the

mass of the hydrogen nucleus will be much smaller than that of the nuclei of the greater mass.

If a first approximation is all that is required, one may consider the hydrogen nucleus as oscillating against an infinitely large mass. Then the vibrational frequency would depend only on the force with which the hydrogen atom is bound to the other atoms. Experimental data have shown that the force constant is of the same order of magnitude for the hydrogen bond whether the hydrogen atom is attached to carbon, oxygen, nitrogen or other heavy groups.

In the search for a characteristic frequency with which to identify a bond, one must consider which type of vibration will be the most variable. The characteristic frequency is best defined for a vibration in which the bond stretches. Thus the bending frequencies are often not as characteristic of a particular bond as other types. The possibilities of resonance must also be taken into account. If there is a possible resonance structure for which the contribution may be large, there often appears a splitting of the characteristic frequency. The greater the number of bonds in a molecule and the stronger the bond in question, the greater the splitting involved.

It must be remembered that if only one bond of a molecule is mathematically treated without considering its relation to the rest of the molecule, the result, at best, will be an approximation.

A few simple symmetrical molecules have been treated mathe-

matically. However, in most cases information must be derived from an empirical treatment of infrared data on several compounds having atomic groups in common. A comparison of spectral curves in this series will show which absorption frequencies are common to all molecules used. By the same method, it may be reasonably assumed for purposes of preliminary calculations that the appearance of a new absorption peak may represent the formation of a new bond.

Discussion of Spectral Data

Two compounds that included a nitrogen atom directly united to a silicon atom were synthesized. The first compound for which infrared data was obtained was described earlier under the discussion of tetraanilinosilane. The resulting spectrum contained two absorption peaks that closely corresponded to frequencies expected of a compound containing an NH_2 group. Since no such group should be present in the molecule if one hydrogen were removed when joining the nitrogen to silicon, the question arose as to whether the isomer, tetra-p-aminotetraphenylsilane, had been prepared.

A search of the literature revealed vastly different physical properties of the isomers. It was stated that the tetra-p-aminotetraphenylsilane requires a difficult four-step synthesis, the product of which melts at 380° C. and is insoluble in all organic media except boiling phenol, aniline, or pyridine. However, the compound analyzed spectrally by this investigator melted

at 243° C. lower than this isomer and was soluble in many organic solvents at room temperature and, in addition, was very unstable towards water, decomposing to give aniline and silicon dioxide. It was felt that this physical and chemical evidence against the preparation of the isomer under the conditions earlier described was very strong but to strengthen the case still more, it was decided to synthesize the second compound, tetra-N-methylanilinosilane, in which there could not possibly be an NH_2 group. The spectrum of this compound was found to have the same absorption frequencies. It was then concluded that the appearance of an absorption peak at the frequency expected of an NH_2 group was a matter of coincidence.

Table 1 contains the absorption frequencies detected by the infrared spectrometer, previously described, for the two silicon-nitrogen compounds and, in addition, those frequencies due to molecules which are similar to structures present in the silicon-nitrogen compounds. Those bands which are listed next to each other are assumed to be due to similar vibrations in each molecular species. In matching those frequencies, the relative shape and trend of each absorption curve were considered as well as the proximity of wave-lengths.

In an attempt to find the characteristic frequency due to a silicon-nitrogen bond, all frequencies exhibited by tetraanilinosilane were listed in the first column of Table 1. In the second column were listed those frequencies due to aniline. All values in the two columns, in addition to those due to the benzene ring

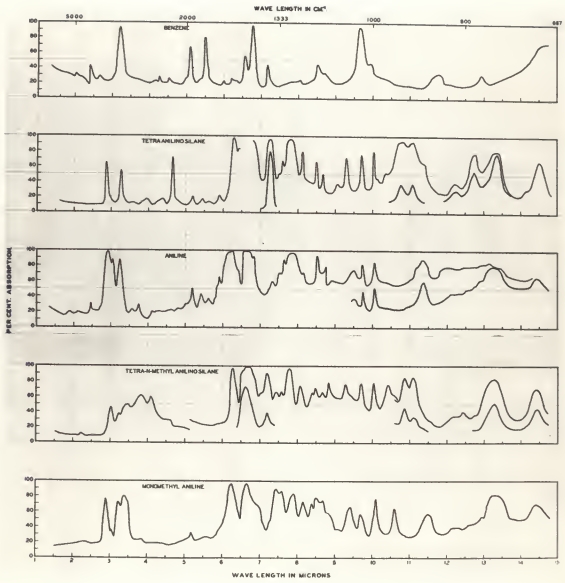


Fig. 3. Infrared spectra of silicon-nitrogen compounds and related groups.

Table 1. Infrared absorption frequencies in microns of silicon-nitrogen compounds and related groups. The amount of absorption is indicated as very strong (VS); strong (S); medium (M); and weak (W).

Tetra-anilino-silane	Aniline	Tetra-N-methylani-linosilane	Monomethyl-aniline	Benzene
	1.90 W			
	2.11 W			2.03 M
		2.26 W	2.32 W	
	2.46 M			2.40 M
				2.66 W
2.86 S	2.93 VS		2.90 S	
	3.04 VS	3.02 M	3.04 M	
3.26 M	3.24 VS	3.23 M	3.22 S	3.21 VS
			3.39 S	
		3.49 M	3.49 S	
3.57 W	3.57 W			
	3.75 W			
		3.82 S	3.83 W	
3.95 W				
	4.11 W	4.08 M		
				4.28 W
4.38 W				
				4.52 W
4.64 S				
5.18 W	5.18 M		5.17 M	5.09 S
5.45 W	5.43 M			5.50 VS
5.61 W	5.61 M		5.58 W	
5.89 W	5.89 S			5.99 W
				6.19 W
6.28 VS	6.28 VS	6.28 VS	6.25 VS	
6.44				6.54 M
continuous	6.70 VS	6.61 VS	6.66 VS	
6.80				6.76 VS
				7.15 M
*7.24 VS		*7.18 VS		
	7.34 M			
		7.42 S	7.43 VS	
VW	7.51 S			
7.58 S	7.64 VS	7.58 S	7.60 VS	
7.82 VS	7.82 VS	7.80 VS	7.90 VS	

Table 1. (concl.).

Tetra-anilino-silane	Aniline	Tetra-N-methylani-linosilane	Monomethyl-aniline	Benzene
		8.07 S		8.02 W
8.12 VS	8.15 S		8.15 S 8.38 S	
8.49 S	8.52 VS	8.48 S	8.50 S	8.51 M
8.67 M	8.70 S	8.65 S	8.67 S	
	8.93 S	8.85 S		
9.06 M				
*9.29		*9.28 S		
			9.42 S	
	9.50 S			
9.70 S	9.73 S	9.71 S	9.68 M	9.65 VS
10.02 S	10.05 VS	10.03 S	10.09 S	
10.14 W				
10.33 M				
			10.59 S	
		10.41 S		
*10.77 VS		*10.86 VS		
*11.07 VS		*11.09 VS		
	11.36 VS			
			11.50 S	
				11.77 M
12.22 M	12.15 S		12.28 M	
*12.72 S		*12.41 S		
				12.91 M
13.34 VS	13.24 VS	13.28 VS	13.32 VS	
14.49 S	14.44 S	14.42 S	14.42 S	14.47 S

* Wave-lengths possibly due to the silicon nitrogen bond. "continuous" indicates a region of total absorption from 6.44 to 6.80 microns that could not be resolved into individual peaks.

that had a close correlation ratio of wave-lengths, were excluded from consideration since they are probably due to other than silicon-nitrogen vibrations. This process of elimination left only a few frequencies that could not be reasonably assigned as due to known atomic groups.

In a like manner those frequencies common to tetra-N-methyltetraanilinosilane and monomethylaniline were rejected as candidates for assignment to the silicon-nitrogen bond.

The wave-lengths listed in Table 1 which are marked with an asterisk are the remaining wave-lengths that could not be reasonably assigned to molecular radicals known to be present in the silicon-nitrogen compound. For convenience in calculations, the near matching values of the unassigned wave-lengths in the two columns were averaged and were found to be 7.21, 9.29, 10.815, 11.08, and 12.56 microns. Of these five absorption frequencies the ones at 10.815 and 11.08 microns exhibited comparatively strong absorption and clear-cut definition. In addition, these two peaks showed negligible wave-length shift when a comparison was made of the spectra of tetraanilinosilane and tetra-N-methylanilinosilane.

A force constant was calculated for each peak as described in Barnes et al., (2) and in Herzberg (9). For example, if the necessary values are substituted into equation 6, one gets

$$902.5 = 1307\ k/9.343$$

$$k = (902.5/1307)^2/9.343$$

$$k = 4.455 \times 10^5 \text{ dynes per centimeter.}$$

The results of these calculations are listed in the following table as calculated according to the references indicated in the parentheses.

Table 2. Force constants as calculated by the methods of Barnes et al., (2) and Herzberg (9).

Microns	: cm^{-1}	: k x 10^5 (2)	: k x 10^5 (9)
10.815	902.527	4.455	4.482
11.08	904.642	4.676	4.706

In silicone compounds the silicon-carbon bond has a force constant of 3.3 x 10^5 dynes per centimeter. According to Herzberg (9) force constants should show a regular increase with an increase in the period of the atoms involved in the bond. Therefore, the force constant for the silicon-nitrogen bond should be slightly larger and of the same order of magnitude as the force constant for the silicon-carbon bond. It may be seen from Table 2 that any of the force constants calculated for the silicon-nitrogen bond would fit this requirement.

In Fig. 3 there are two curves for tetra-N-methylanilinosilane in the range of 10.5 to 11.5 microns. The upper curve shows almost complete absorption in this range of wave-lengths. Under these conditions it is difficult for the automatic recording device on the spectrograph to differentiate between the small amounts of transmitted energies. Therefore, a much thinner sample was placed in the instrument to obtain better definition. The resultant curve for this sample is drawn directly below the

upper curve, and shows the absorption peak at 10.815 microns to be relatively the stronger absorption. Therefore, this wavelength was chosen as representing the characteristic or fundamental frequency of the silicon-nitrogen bond. This appears to be a reasonable assumption since many silicon-carbon characteristic stretching frequencies are found in this general region.

The formula used to calculate the energy of dissociation requires the use of the equilibrium frequency of oscillation, ω_e, which may be calculated from the observed fundamental frequency, ω, according to equation 3. Substitution of 10.815 microns into this formula gives an equilibrium frequency of 912.915^{-1}.

To obtain an energy of dissociation for the silicon-nitrogen bond the above calculated value for the equilibrium frequency may be substituted into the following formula:

(17) $$D_o = (1/4)hc\omega_e\ (1/x - 2)$$

where ω_e is the equilibrium frequency and x is the anharmonicity. The anharmonicity was the only unknown quantity necessary for solution of the above equation.

A careful study of Table 36 in Herzberg (9) revealed that the bond formed between silicon and other elements exhibits a general increase in the amount of anharmonicity, x, as the weight of the atoms increases. In an attempt to correlate the amount of anharmonicity with some elemental property, the amount of anharmonicity of bonds given in this table were plotted against various properties such as atomic weights within each periodic group, atomic weights within each periodic series, electro-

negativity, atomic radii, number of closed shells and the number of electrons in open shells. Of these, the graph on which anharmonicity was plotted against atomic weights within each periodic series seemed to show the best hope for correlation of properties. An outline of this graph is shown in Fig. 4. A collection of known values for various bonds is listed in Table 3. A study of Fig. 4 reveals a regular increase in anharmonicity within each series of elements with an increase in atomic weight. A single discrepancy is shown if the value for the silicon-nitrogen bond as given in Herzberg is plotted on the same scale. If anharmonicity is at least in part a function of atomic weight within each series, then one would expect its representatives position on the graph to lie directly on an extrapolation of the line connecting the positions of fluorine and oxygen with the ordinate representing the atomic weight of nitrogen. Since the value given in Herzberg does not agree with this extrapolation, one might conclude that either the behavior of the silicon-nitrogen bond is anomolous or that the data as given in Herzberg does not, for some reason, conform to that predicted by this extrapolation. Since the value given in Herzberg had been checked by reliable investigators, it was decided to use both the given and the extrapolated values for anharmonicity in calculating the energy of dissociation of the silicon-nitrogen bond. Extrapolation of the line for series two to the position representing the atomic weight of nitrogen gave a value of 0.00440 for the anharmonicity of the silicon-nitrogen bond. This is lower than the

Table 3. Collected constants for the electronic ground states of known diatomic molecules.

Molecule	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_o (e-volt)	k x 10^5 (dynes/cm.)
SiBr	425	1.5	3.7	
SiCl	535	2.2	4.2	2.6
SiF	857	4.7	4.8	5.6
SiH	2080			
SiO	1242	6.05	7.4	
SiS	749	2.56	6.2	
SiSe	580	1.78	5.8	
SiTe	480	1.16	5.5	
CH	2824	46.0	3.47	4.76
SiC				3.31
SiR				3.14
CN	2069	13.14	5.96	
CC				5.14
CR				4.71
CO	2168	13.04	9.14	
CSe	1051	8.0	4.0	
CF				4.0
CS	1285	6.5	7.8	

Table 4. Types of data used in calculation of silicon-nitrogen bond energies and corresponding values in kcal per mole.

thermochemical		70-90
infrared spectra	x = .005696	113.34
infrared spectra	x = .00440	147.115
violet spectra		143

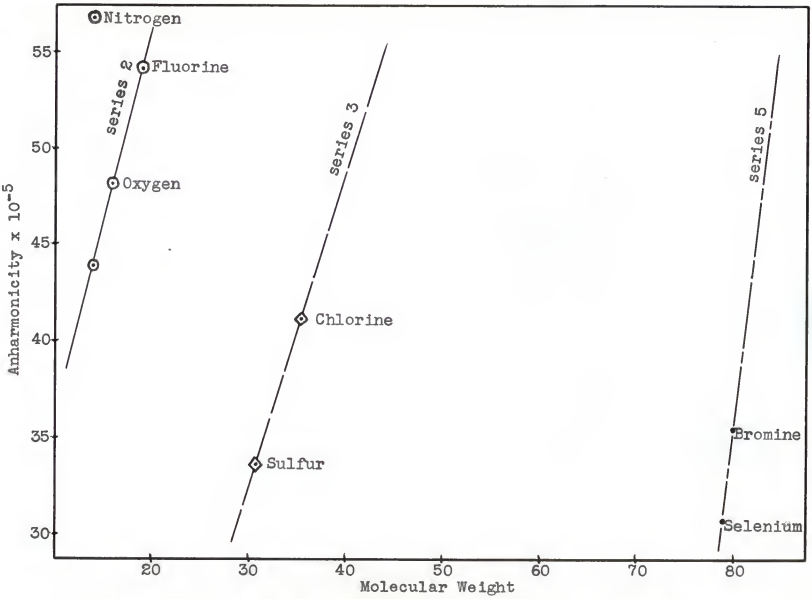


Fig. 4. Molecular weight plotted against anharmonicity of diatomic molecules including silicon and series 2, 3, and 5 elements.

value of 0.005695 recorded in Herzberg. Use of 0.005696 for x in equation 17 gave a dissociation energy for the silicon-nitrogen bond of 113.34 kcal per mole. Substitution of the value of 0.00440 into the same equation gave a result of 147.115 kcal per mole. It may be seen from Table 4 that this value very closely corresponds to the value derived from the violet spectrum of a nitride of silicon. It would seem that the value for anharmonicity derived from extrapolation of the series two line is approximately a correct one.

Values for the dissociation energy of the silicon-nitrogen bond derived from thermochemical data are much lower than any of the results obtained from spectral data. Even though a number of simplifying assumptions must be used in calculations from spectral data, the results, in general, are more reliable than thermochemical data. Therefore, it was decided that the extrapolated value, 0.00440, for the anharmonicity of the silicon-nitrogen bond together with the corresponding value of 147.115 kcal per mole for the dissociation energy of the silicon-nitrogen bond most closely represented the true picture of this bond.

Bichowsky and Rossini (3) recorded the heat of formation of Si_3N_4 as 157 kcal. The structure of the molecule was not given in this reference. The original article gave no hint concerning the molecular configuration of this Si_3N_4. Since the number of silicon-nitrogen bonds present in this molecule is either not clear, or not as yet established, the value of 157 kcal is of little use in this discussion.

The magnitude of energy possessed by the bond at the absolute zero of temperature may be of interest in a theoretical discussion. Therefore, this energy was calculated with the aid of the following equation:

(18) $$E_o = 1/4\ h\omega_e\ (2 - x)$$

The zero point energy was found to be approximately 1.3 kcal per mole.

SUMMARY

Some compounds containing a silicon atom directly united to a carbon atom were prepared. The analytical data seemed to lend support to the postulated formulas.

By comparison of the infrared spectra of these compounds with the spectra of related molecular groups, some frequencies were found that may possibly be due to the silicon-nitrogen bond. One of these frequencies, 902.527 cm^{-1}, was selected as the probable fundamental frequency. By use of this frequency in appropriate formulas, a force constant was calculated for the silicon-nitrogen bond. This force constant was determined to be 4.468×10^5 dynes per centimeter. In an effort to correlate physical properties of atoms linked to silicon with the anharmonicity of those bonds, an extrapolation of a line representing anharmonic values plotted against atomic weight was used. By this method anharmonicity of the silicon-nitrogen bond was tentatively assessed to be 0.00440. The equilibrium frequency, 912.915 cm^{-1}, that was calculated from the proposed fundamental frequency was used to calculate an ap-

proximate energy of dissociation of 147 kcal per mole for the silicon-nitrogen bond in tetraanilinosilane and tetra-N-methylanilinosilane. An approximate zero point energy was found to be 1.3 kcal per mole.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. A. C. Andrews, major instructor, for understanding encouragement, instruction and support before and during this investigation; to Dr. S. E. Whitcomb of the Department of Physics for instruction in the techniques of infrared spectroscopy, for information on methods used in the interpretation of data and for the use of the spectrometer and materials; to Dr. R. E. Silker, Head of the Department of Chemistry, for making possible the work of this investigator; to Dr. R. D. Dragsdorf of the Department of Physics for his work in an attempt to obtain X-ray data; and to Mr. C. C. Blood for supplying the apparatus and chemicals necessary during this study.

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